SUPPORTING INFORMATION

Carbon-Sulfur Bond Strength in Methanesulfinate and Benzenesulfinate Ligands Directs Decomposition of Np(V) and Pu(V) Coordination Complexes

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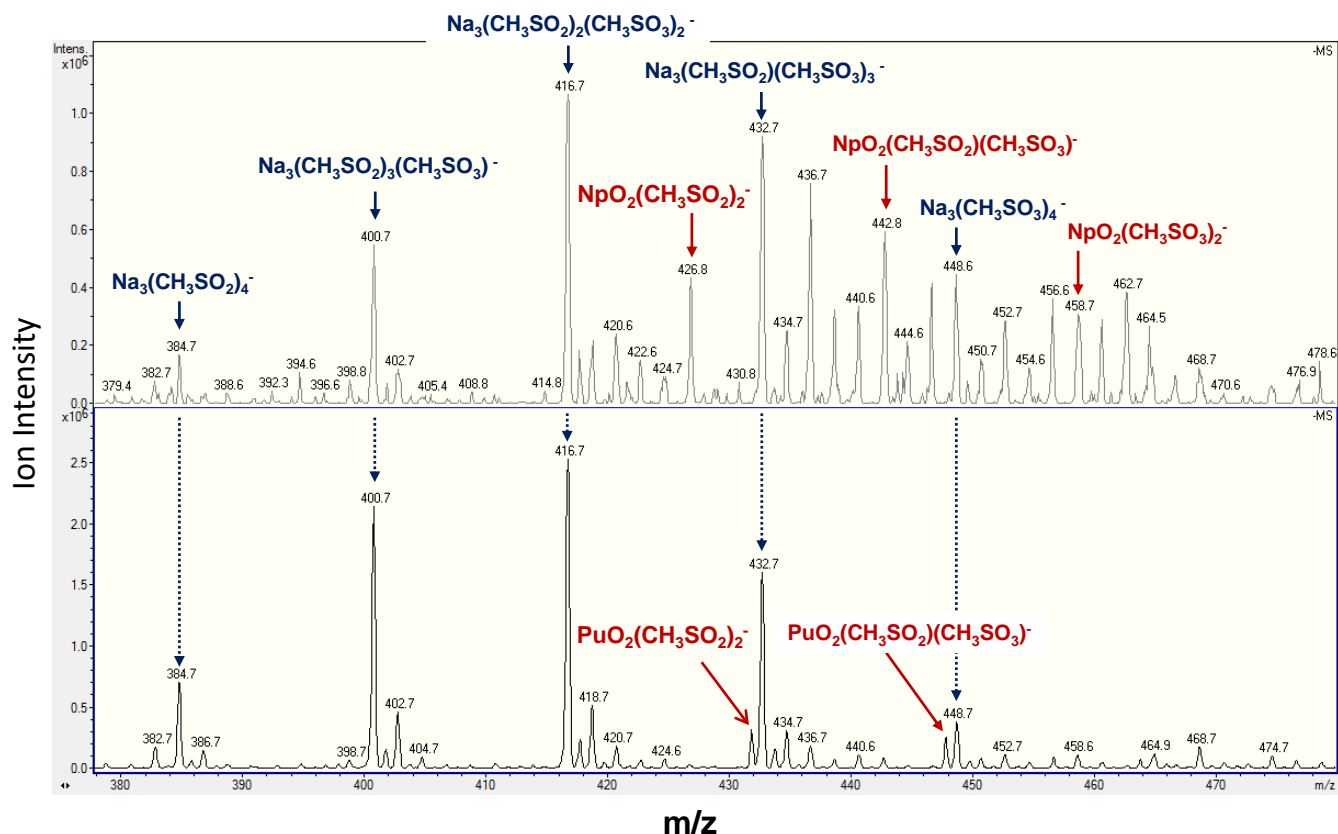
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Figure S1. Representative ESI mass spectra for the $An^{VI}O_2(ClO_4)_2$ / CH_3SO_2Na solutions for An = Np (top) and An = Pu (bottom). It is likely that partial or predominant reduction of Np(VI) to Np(V), and/or Pu(VI) to Pu(V) (or to even lower oxidations states) had occurred prior to or during ESI. Dominant ESI species are the indicated clusters containing sodium added to the solutions as the source of sulfonate. In addition to the expected methane sulfinate ($CH_3SO_2^-$) complexes are unexpectedly abundant species containing methane sulfonate ($CH_3SO_3^-$), possibly partly due to oxidation of sulfonate by the actinyl(VI) species. For the reported CID experiments the species of interest, $Np^VO_2(CH_3SO_2)_2^-$ or $Pu^VO_2(CH_3SO_2)_2^-$, was isolated from other ESI species. A contrast with previous results for uranyl is the absence here of the An(VI) complexes $An^{VI}O_2(CH_3SO_2)_3^-$ for An = Np and Pu; this species was abundant for An = U. The species in the ESI mass spectra thus clearly reveal the substantially higher An(VI/V) reduction potentials for An = Np (+1.16 V) and Pu (+0.94 V) versus An = U (+0.09 V).
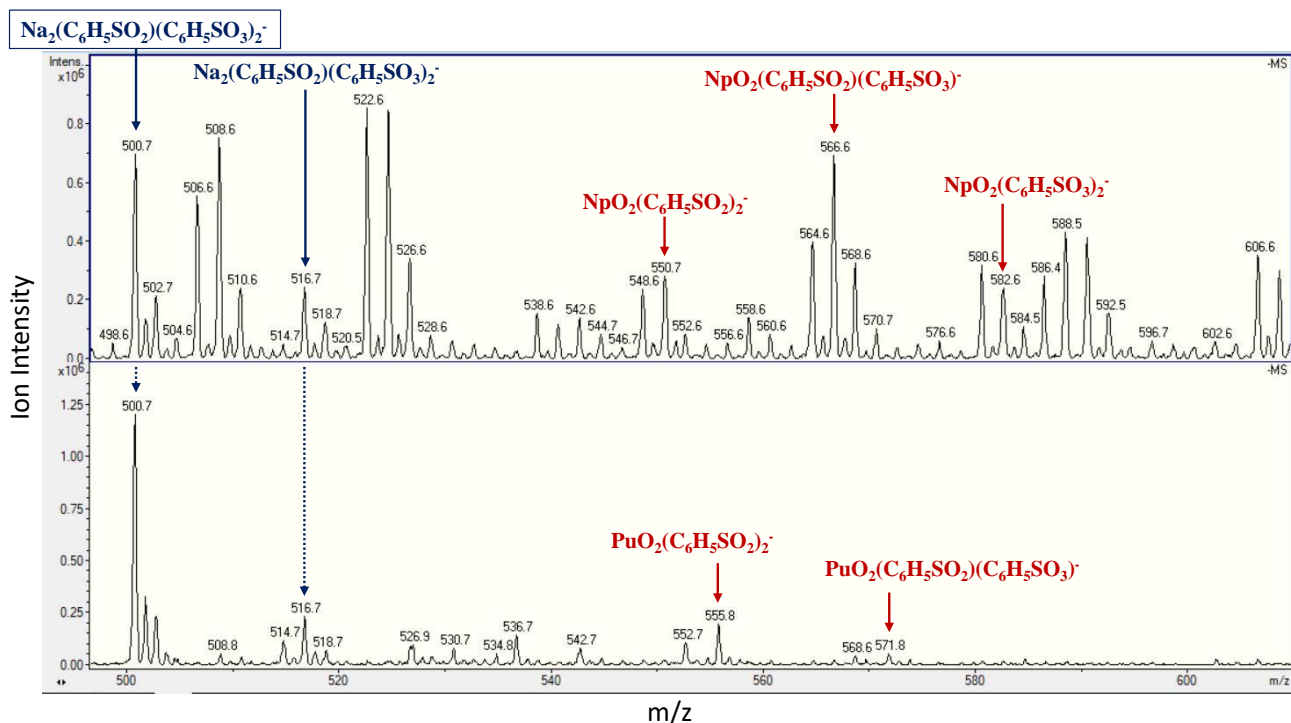
Figure S2. Representative ESI mass spectra for the $An^{VI}O_2(ClO_4)_2$ / $C_6H_5SO_2Na$ solutions for An = Np (top) and An = Pu (bottom). For the reported CID experiments the species of interest, $Np^VO_2(C_6H_5SO_2)_2^-$ or $Pu^VO_2(C_6H_5SO_2)_2^-$, was isolated from other ESI species.
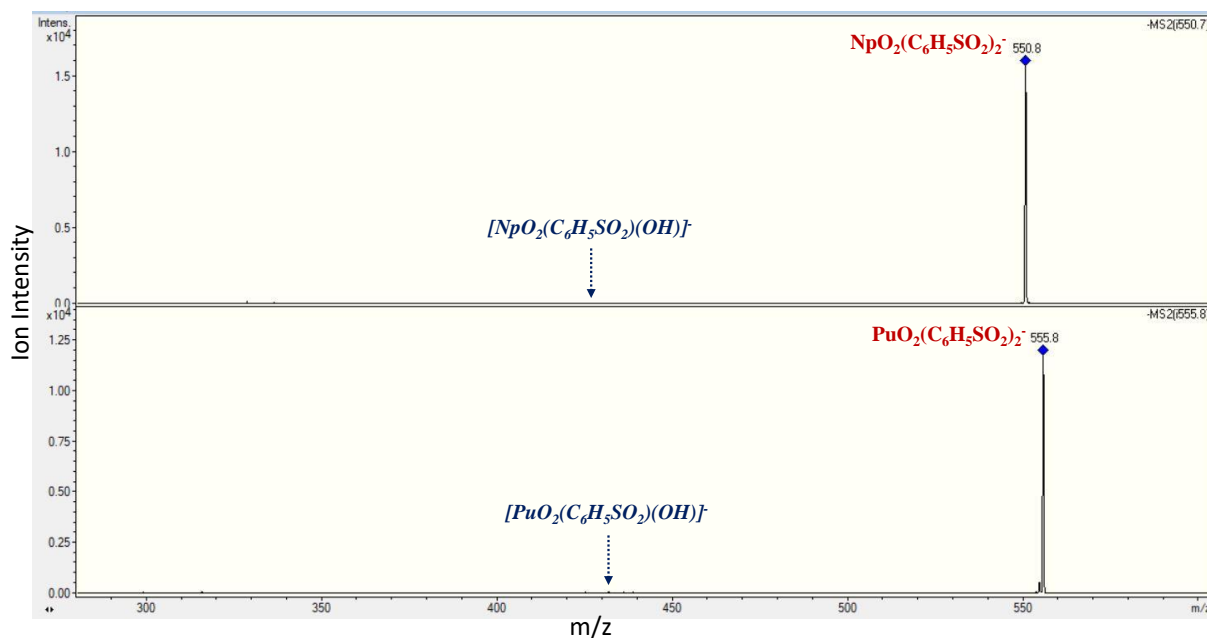
Figure S3. Mass spectra obtained after isolating $NpO_2(C_6H_5SO_2)_2^-$ (top) and $PuO_2(C_6H_5SO_2)_2^-$ (bottom with no applied CID voltage. The absence of detectable product peaks substantiates that the results apparent in Figure 4 are due to CID rather than spontaneous reaction.
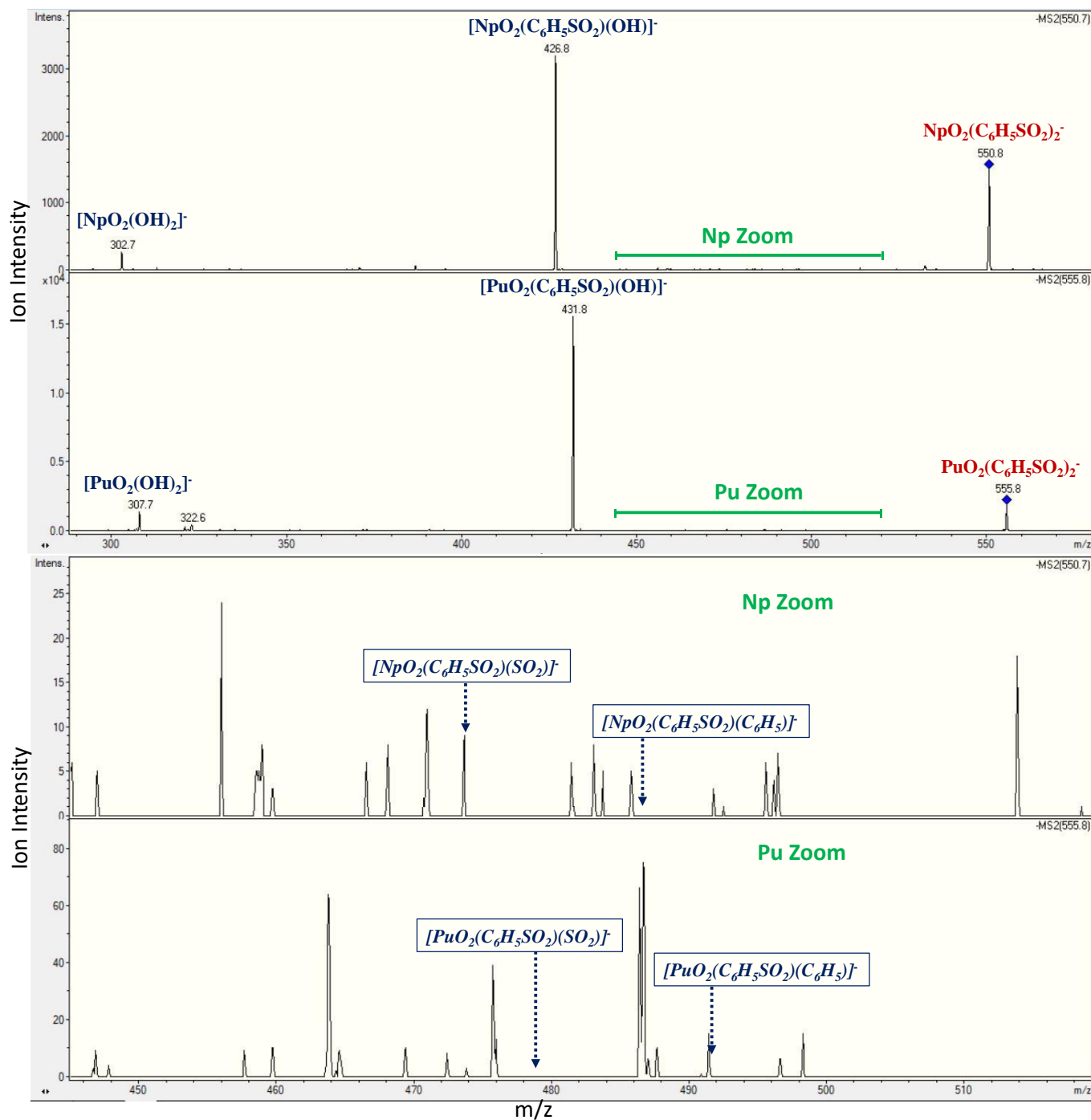
Figure S4. CID mass spectra for $NpO_2(C_6H_5SO_2)_2^-$ and $PuO_2(C_6H_5SO_2)_2^-$; these are the same data as shown in Figure 4. The bottom two spectra are y-axis expansions ("Zooms") of the m/z range indicated by green lines. The indicated potential products in the bottom spectra were not detected; the minor feature near the m/z for $[NpO_2(C_6H_5SO_2)(SO_2)]^-$ is essentially at the background noise level. The small peak close that expected for $[PuO_2(C_6H_5SO_2)(C_6H_5)]^-$ is actually 0.4 m/z below the m/z corresponding to this species.

(a)

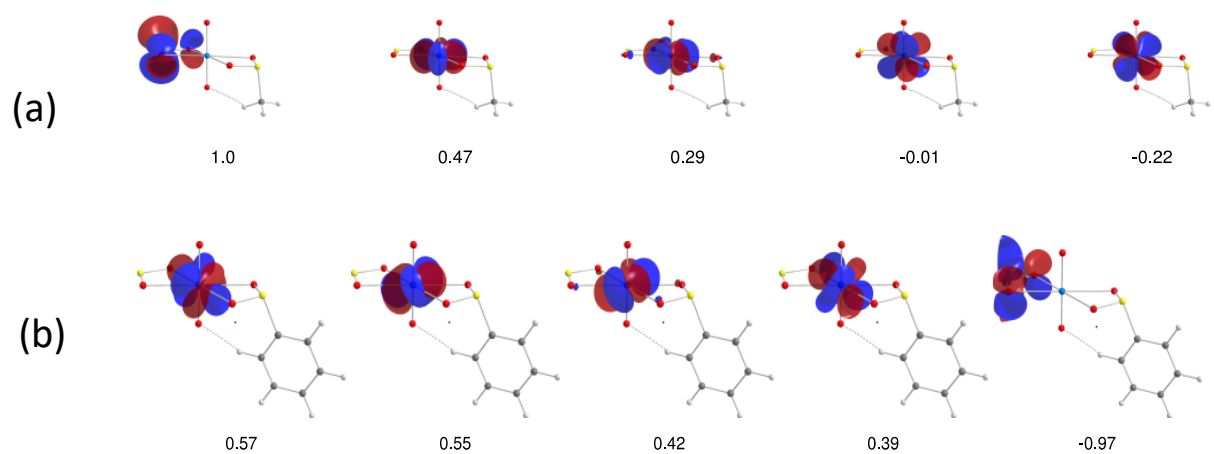| 1.0 | 0.47 | 0.29 | -0.01 | -0.22 |

(b)

| 0.57 | 0.55 | 0.42 | 0.39 | -0.97 |

Figure S5. Selected Natural Spin Orbitals NSOs along the z-O_{yl} direction for SO ground state of (a) $[UO_2(CH_3SO_2)(SO_2)]^-$ and (b) $[NpO_2(C_6H_5SO_2)(SO_2)]^-$. The corresponding occupation numbers n_z are given. Isosurface values: ±0.03 au.

Table S1. Reaction enthalpies ΔH_r at 298.15 K in eV for reactions (8) to (11) computed at various levels of theory. The spin-orbit contribution (Δ) is in parenthesis.

Reaction	B3LYP	B3LYP[9]	PBE0	CASSCF	PT2	PT2+SO (Δ)
			Uranyl			
(8)	1.79	1.68	2.03	1.49	1.85	1.84 (-0.01)
(9)	-0.50	-0.19	-0.35	0.54	-1.27	-0.95 (0.33)
(10)	2.14	N/A	2.37	1.85	2.39	2.37 (-0.02)
(11)	1.24	N/A	1.22	1.49	1.51	1.51 (0.00)
			Neptunyl			
(8)	N/A	N/A	2.02	1.47	1.83	1.81 (-0.01)
(9)	N/A	N/A	-0.10	-0.56	-0.49	-0.38 (0.33)
(10)	N/A	N/A	2.35	1.85	2.32	2.34 (-0.02)
(11)	N/A	N/A	1.30	1.57	1.57	1.55 (0.00)
			Plutonyl			
(8)	N/A	N/A	2.00	1.46	1.68	1.71 (0.03)
(9)	N/A	N/A	0.29	-0.55	-0.25	0.01 (0.26)
(10)	N/A	N/A	2.50	1.93	2.14	2.27 (0.13)
(11)	N/A	N/A	1.40	1.64	1.64	1.61 (-0.03)